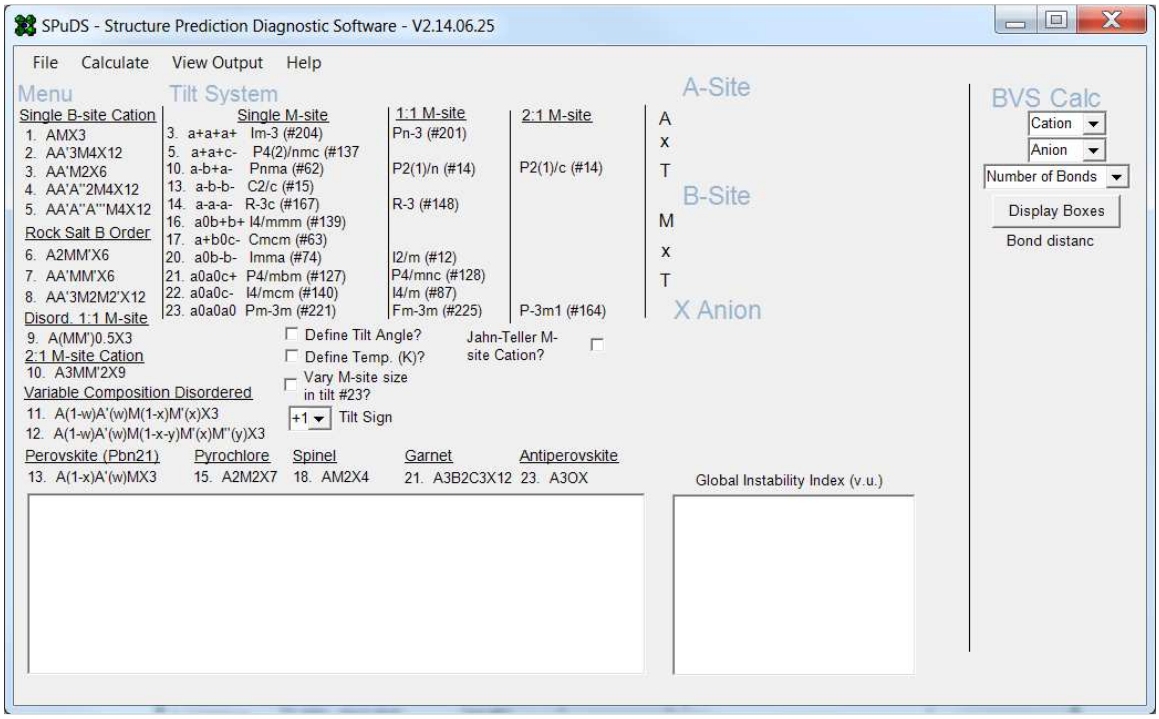
SPuDS Users Guide



Written and developed by

Dr. Michael W. Lufaso
e-mail: michael.lufaso@unf.edu

Dr. Patrick Woodward
e-mail: woodward@chemistry.ohio-state.edu

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Preface

Disclaimer

By downloading the software programs *SPuDS (Structure Prediction Diagnostic Software)* and (*TUBERS)* (*Tilting Using Basic Equation Relationship Software*), you agree to the terms and conditions concerning its use specified in the license agreement that is provided as part of the distribution. The Software is provided to End User on an as is basis. No user support is provided or implied. No warranty, express or implied to end user or to any other person or entity is made.

Acknowledgements

MWL would like to thank Dr. Patrick Woodward in the initialization and assistance throughout the development of *SPuDS*. Resources provided by the Ohio State University, Columbus, OH are acknowledged. Discussions with I.D. Brown (McMaster University) are appreciated.

Using SPuDS

Publication of results obtained using the program *SPuDS* or *TUBERS* should state that *SPuDS* and/or *TUBERS* were used and contain the following reference:

M.W. Lufaso, P.M. Woodward, (2001) "The Prediction of the Crystal Structures of Perovskites Using the Software Program SPuDS" *Acta Cryst.*, B**57**, 725-738.

Requests

Requests for additional features (*e.g.* multiple doping levels on A- and M-site), additional explanations in the User Manual, tilt angle calculation or any other additional comments and questions may be addressed to Michael Lufaso (michael.lufaso@unf.edu) and Patrick Woodward (woodward@chemistry.ohio-state.edu). The software is continually under development, but research areas that are requested will be addressed first.

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Chapter 1

Introduction

1.1 Overview of SPuDS

The software program SPuDS has been developed to predict the crystal structures of perovskites, including those distorted by tilting of the octahedra. The user inputs the composition and SPuDS calculates the optimal structure in ten different Glazer tilt systems for single M-site cations and six for 1:1 rock-salt ordered double perovskites. This is performed by distorting the structure to minimize the global instability index, while maintaining rigid octahedra. The location of the A-site cation is chosen so as to maximize the symmetry of its coordination environment. In its current form SPuDS can handle up to four different A-site cations in the same structure and two octahedral ions. Structures predicted by SPuDS are compared with a number of previously determined structures to illustrate the accuracy of this approach.

Additional details may be found on the following webpage.
http://www.unf.edu/~michael.lufaso/spuds/index.html

1.2 Installation

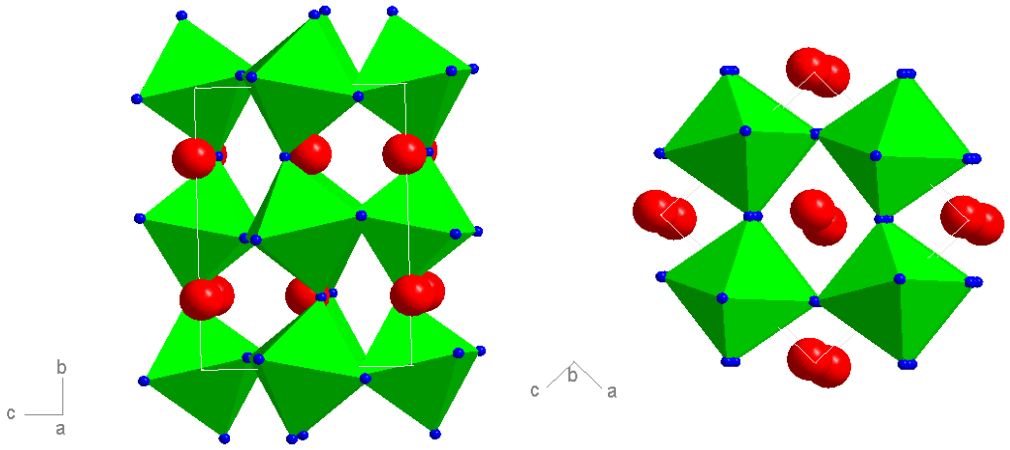
Click the setup.exe file and install in any folder of your choice. The default location for installation is C:\Program Files\SPuDS\. Note that you will need to open the folder containing the spud.exe and tubers.exe files to examine the output files or any log files. Copy and rename the output.txt file to keep to calculated crystal structure for later comparison. If you experience error messages regarding "MSVBVM60.DLL file not found", then unzip the Visual Basic run-time DLL msvbvm60.zip to the Windows\system (95,98,ME) or Windows\system32 (XP) if it not already installed on your PC. Restart the computer, and then execute SPuDS again.

1.3 Octahedral Tilting Notation

Octahedral tilting reduces the symmetry of the A-site cation coordination environment and results in a change in A-X bond lengths. However, there are multiple ways in which the octahedra can tilt, each leading to a different coordination environment for the A-site cation(s). A standard notation has been developed to describe octahedral tilting distortions in perovskites by Glazer (1972). The notation describes a tilt system by rotations of MX_6 octahedra about any of three orthogonal Cartesian axes, which are coincident with the three axes of the aristotype cubic unit cell. The notation specifies the magnitude and phase of the octahedral rotations. The letters in Glazer notation indicate the magnitude of the rotation about a given axis, e.g., the letters a, b, and c imply unequal tilts about the x, y, and z axes. A superscript is used to denote the phase of the octahedral tilting in neighboring layers. A positive superscript would denote the neighboring octahedra tilt in the same direction (in-phase) and a negative superscript implies the tilts of neighboring octahedra tilt in the opposite direction (out of phase). A superscript of 0 signifies no tilting about that axis. Rotation of one octahedron causes the four adjacent octahedra in the same layer to rotate in the opposite direction in the same angle. Lattice connectivity is such that rotations of the octahedra in the layer above and below are not

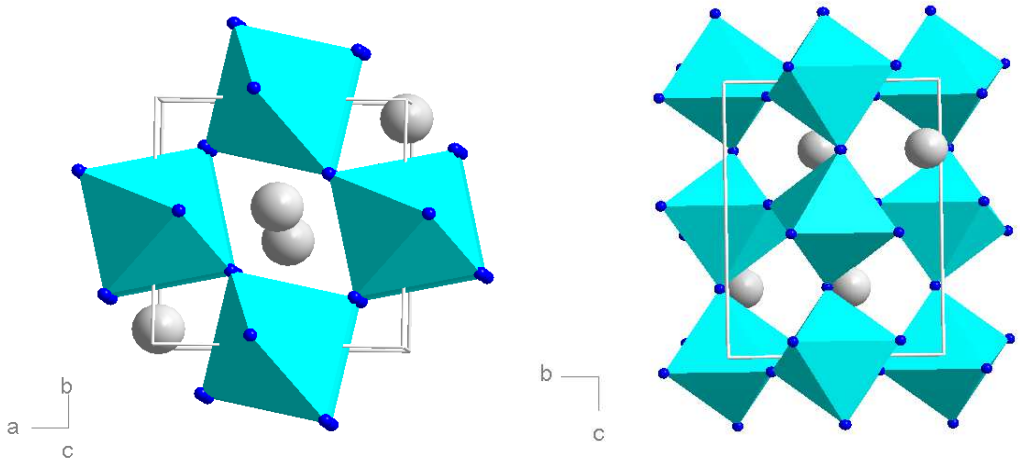
geometrically constrained to the initial rotation and can occur in phase (+ superscript) or out of phase (- superscript) with respect to the first octahedral layer. The tilting of the octahedra reduces the symmetry of the undistorted perovskite tilt system a0a0a0. Glazer derived 23 different tilt systems, which lead to 15 different space groups. There are 15 tilt systems that can occur in real crystals, each with a different space group for simple perovskites. Ordered double perovskites, $A_2MM'O_6$, have also been described by the Glazer tilting notation.

The order of the tilting notation is somewhat arbitrary in crystal structures which don't have the crystallographic axis parallel to the M-X-M bonds. For example, consider a perovskite in space group *Pnma* (tilt system #10, $a^-b^+a^-$). Looking down the a-axis one notices, because of the $\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$ cell size relative to the aristotype cubic unit cell, it does not correspond to any of three orthogonal Cartesian axes which are coincident with the three aristotype axes. However, looking down the b-axis it is readily apparent that the octahedral tilting is in-phase (+). The out of phase tilting is in the ac-plane, so $a^-b^+a^-$ would be a logical choice.

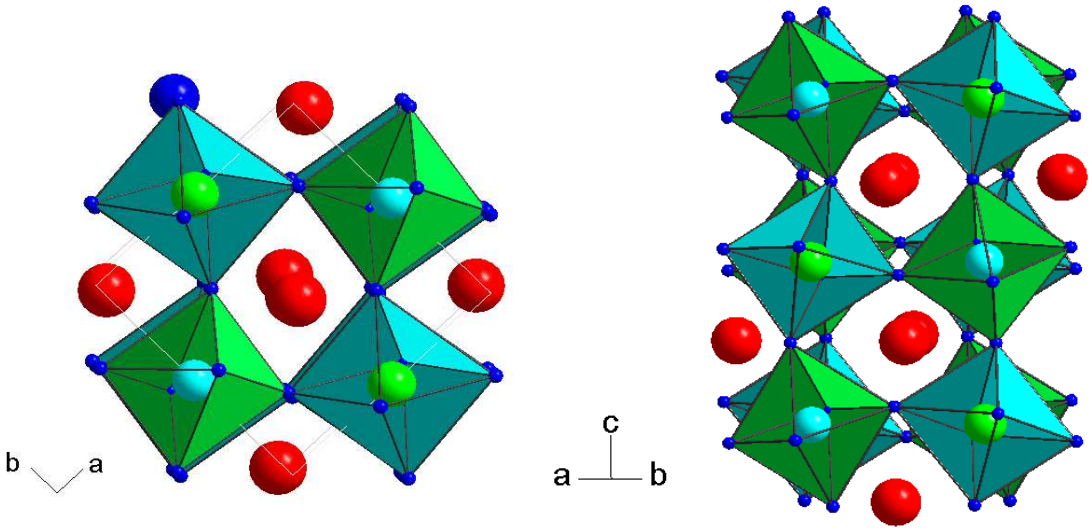


Space group *Pnma* perovskite ($a^-b^+a^-$) #10.

Perovskites crystallizing in space group *Pbnm* are better described by the tilting notation $a^-a^-b^+$. An example is shown below. Similarly, 1:1 ordered double perovskites in space group $P2_1/n$ are best described by octahedral tilting notation $a^-a^-b^+$ (#10).



Space group *Pbnm* perovskite ($a^-a^-b^+$) #10.



Space group $P2_1/n$ perovskite ($a^-a^-b^+$) #10.

1.4 SPuDS Calculation Algorithm

A brief description of the calculation algorithm is given, however the interested reader is referred to Lufaso & Woodward (2001) for a more detailed description. Additions to the software have been added that are not part of the version 1 of the software. SPuDS Calculation Procedure

Optimization of the crystal structure in an unconstrained manner requires determination of the unit cell dimensions and all free positional parameters. In order to simplify this process SPuDS restricts the octahedra to remain rigid (six equivalent M-X distances and all X-M-X angles equal to 90º). This seems to be a reasonable restriction in light of the fact that most distorted perovskites show very little distortion of the MX_6 octahedra, though obviously SPuDS will not work well in systems where octahedral distortions are expected. Once this restriction is in place the full crystal structure can be

generated from two variables: the size of the octahedron and the magnitude of the octahedral tilting distortion. Additional degrees of freedom must be taken into consideration in those tilt systems where either the A-cation does not sit on a fixed position (e.g., $a^-b^+a^-$) or octahedral distortions cannot be avoided ($a^+a^+c^-$). SPuDS calculates the fractional position of each atom at each tilt angle step over a wide range of octahedral tilt angles. The initial optimization is coarse to allow a wide range of structures to be calculated quickly and the tilt angle increment is finer for successive (3-5) optimization routines resulting in a determination of the optimal tilt angle.

The size of the octahedron and the optimum magnitude of the octahedral tilting distortion are calculated utilizing the bond valence model, which is used to quantitatively describe inorganic bonding in ionic solids (Brown, 1978). The bond valence, s_{ij}, associated with each cation-anion interaction is calculated using

$$S_{ij} = e^{[(R_{ij}-d_{ij})/B]}$$

, where d_{ij} is the cation-anion distance. The B parameter is empirically determined, but can often be treated as a universal constant with a value of 0.37. R_{ij} is empirically determined for each cation-anion pair based upon a large number of well-determined bond distances for the cation-anion pair in question. SPuDS uses modern bond valence parameters from Brown, 2004. The atomic valences, V_i(calc), of the A and M cations and X anion are calculated by summing the individual bond valences (sij) about each ion.

$$V_{i(calc)} = \sum_j S_{ij}$$

Six nearest neighbor anions are used for the M cation, six nearest neighbor cations for the X anion and twelve nearest neighbor anions for the A-site cation are used in the calculations. No assumption is made about the coordination number of the A-site cation (valences for twelve A-X interactions are calculated in all cases), but the contribution to the atomic valence sum becomes smaller as the A-X bond distance increases. The B cations remain at fixed positions in all space groups generated by simple tilting of the MX_6 octahedra. The M-X bond distance, which determines the size of the octahedron, is calculated so as to optimize the bond valence sum of the octahedral cation. The X-M-X bond angles of the MX_6 octahedra remain ideal (90°) and the M-X bond distances are held constant in the calculations. The valence sum of the A-site cation is varied by changing the size of the octahedral tilting distortion.

The optimized structure is one where the difference between the calculated bond valence sum and the formal valence (equal to its oxidation state) of each ion is minimized. This value, which is termed the discrepancy factor (Rao *et al*, 1998), d, is a measure of the lattice strains present in the compound. The discrepancy factor is calculated according to

$$d_i = V_{i(ox)} - V_{i(calc)}$$

, where Vi(ox) is the formal valence and Vi(calc) is the calculated bond valence sum for the ith ion. The overall structure stability is determined by comparing the calculated bond valence sums with the ideal formal valences. This quantity is referred to as the global instability index (GII) and is calculated according to (Salinas-Sanchez, 1992):

$$GII = \sqrt{\frac{\sum_{i=1}^{N}\left(d_i^2\right)}{N}}$$

The variables involved in the GII equation are discrepancy factor (d_i) and N, which is the number of atoms in the formula unit. During the optimization process the octahedral tilt angle is stepped incrementally and the individual *A*-*X* and *M*-*X* bond distances, discrepancy factors and global instability index are calculated at each step. After the first optimization process, the procedure is repeated using smaller tilt angle increments in order to minimize the GII. The stability of perovskite compositions with different atoms, symmetry, tilt systems and structure can be evaluated by comparing the GII. The GII value is typically <0.1 valence units (v.u.) for unstrained structures and as large as 0.2 v.u. in a structure with lattice induced strains. Crystal structures with a GII greater than 0.2 v.u. are typically found to be unstable, and reports of such structures are usually found to be incorrect.

Chapter 2

Crystal Structure Calculation

2.1 Simple Calculation Instructions

The SPuDS software is composed of several menus. User input is required at each of these steps described below.

Menu

Menu 1 allows stoichiometry selection for single M-site cations simple perovskites, 1:1 ordered double perovskites, and disordered perovskites. Select the menu by clicking the number of the formula of interest (1-23). A box will appear with the menu number.

Tilt System

Menu 2 selects the tilt system for which the output results will be displayed. A further description of the Glazer notation may be found in the literature and in the paper detailing the first version of SPuDS. Click the number of the tilt system of interest, or choose **23** for the untilted perovskite. A box will appear with the number of the tilt system. At this point the appropriate boxes for the A-site and M-site cation will appear.

Formula

Input of the ions and oxidation states is performed by clicking the drop down boxes that appear depending on the Menu selection. Selection the ions and the oxidation states for each of the cations and anions.

'Calculate'

Clicking calculate passes the entered values to the calculation subroutines. Note that error checking may not determine all errors in the input and crash the software. E-mail the author if a problem persists.

Options

Define Tilt Angle?

Certain tilt systems (currently # 22, 21, 20, 17, 16, 14, 10, 3) with a single B-site cation) allow the user to define the tilt angle instead of SPuDS calculating the bond valence sum optimized tilt angle. In general this box should be unchecked.

Define Temperature?

Click the check box to define the temperature. This option changes the bond distances calculated from the bond valence parameters. The default temperature is 298 K.

Vary M-site in #23?

Allows M-site expansion in tilt system number 23 (space groups *Fm-3m* and *Pm-3m*).

Tilt Sign

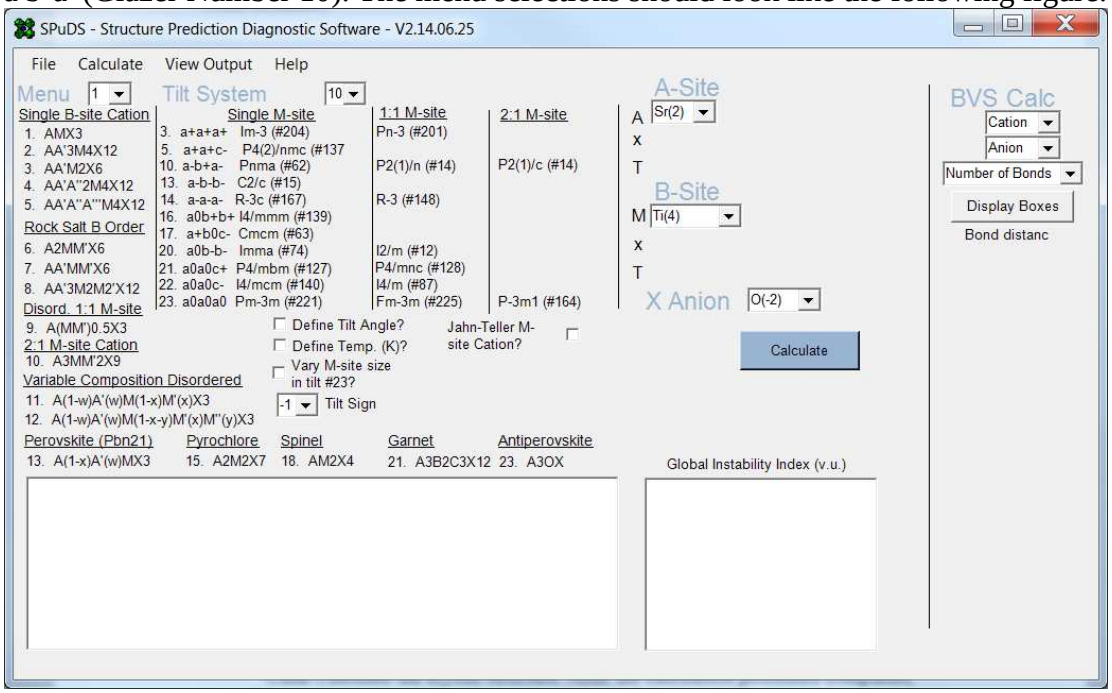
Adjusts the phase of the tilt angle (positive or negative). This option is not implemented in all tilt systems.

Jahn-Teller M-site cation?

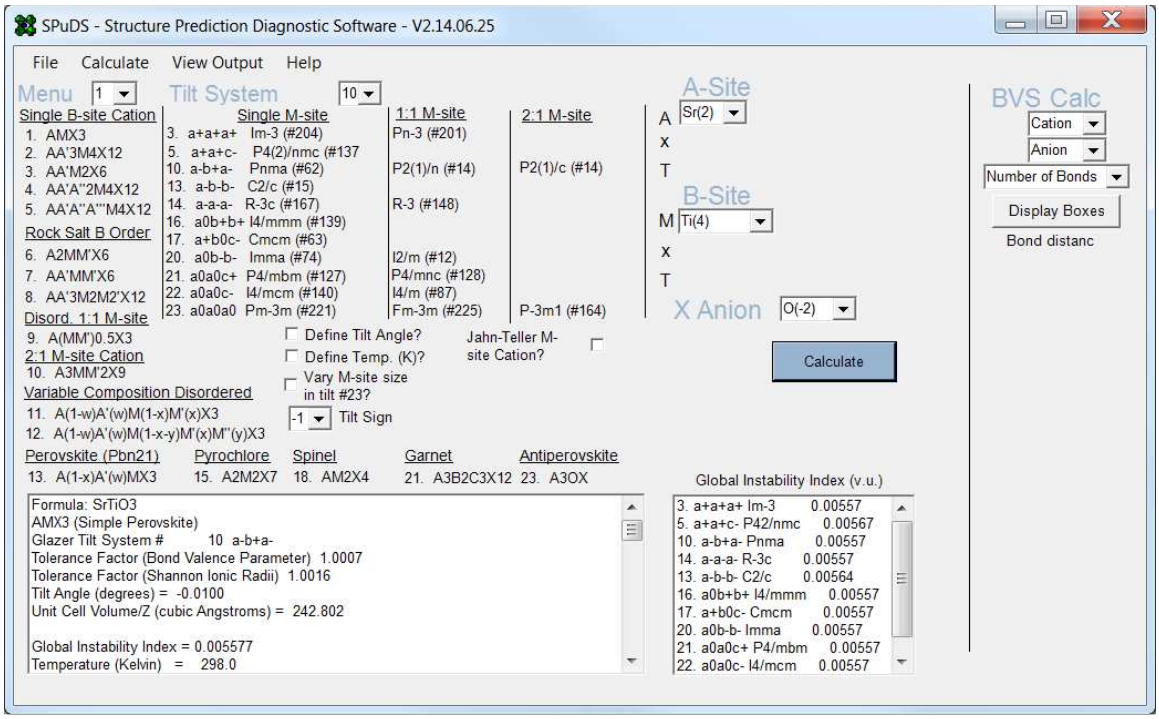
Allows for using a Jahn-Teller distorted cation (*e.g.* Mn^{3+}) with unequal M-X bond distances.

2.2 Sample Calculation of $CaTiO_3$

The mineral perovskite $CaTiO_3$ crystallizes in space group *Pnma* in tilt system $a^-b^+a^-$ (Glazer Number 10). The menu selections should look like the following figure.



Click Calculate the crystal structure. After the calculation procedure completes, the software should display the results shown in the next figure.



2.3 Output files

Several output files are prepared and described below.

2.3.1 output.txt

This file is shown in the SPuDS main output box. It contains most of the useful crystal information. The formula, Glazer tilt notation, tolerance factor calculated from ionic radii and bond valence method, octahedral tilt angle, unit cell volume, Global Instability Index, temperature of the calculation, bond valence sums, Wyckoff site occupancies, space group, lattice parameters, fractional coordinates, bond distances and valences, and M-O-M bond angles.

2.3.2 gii.txt

This file contains the calculated GII for each of the tilt systems. This is displayed in the rightmost box of the *SPuDS* program. These values can be used to compare the relative stability for each tilt system. Note the lowest GII does not necessarily indicate the most likely tilt system. If the GII is below a certain threshold, effects not considered in these calculations are the driving for towards crystallization in a particular space group and tilt system.

2.4 Variable Temperature Crystal Structure Calculation

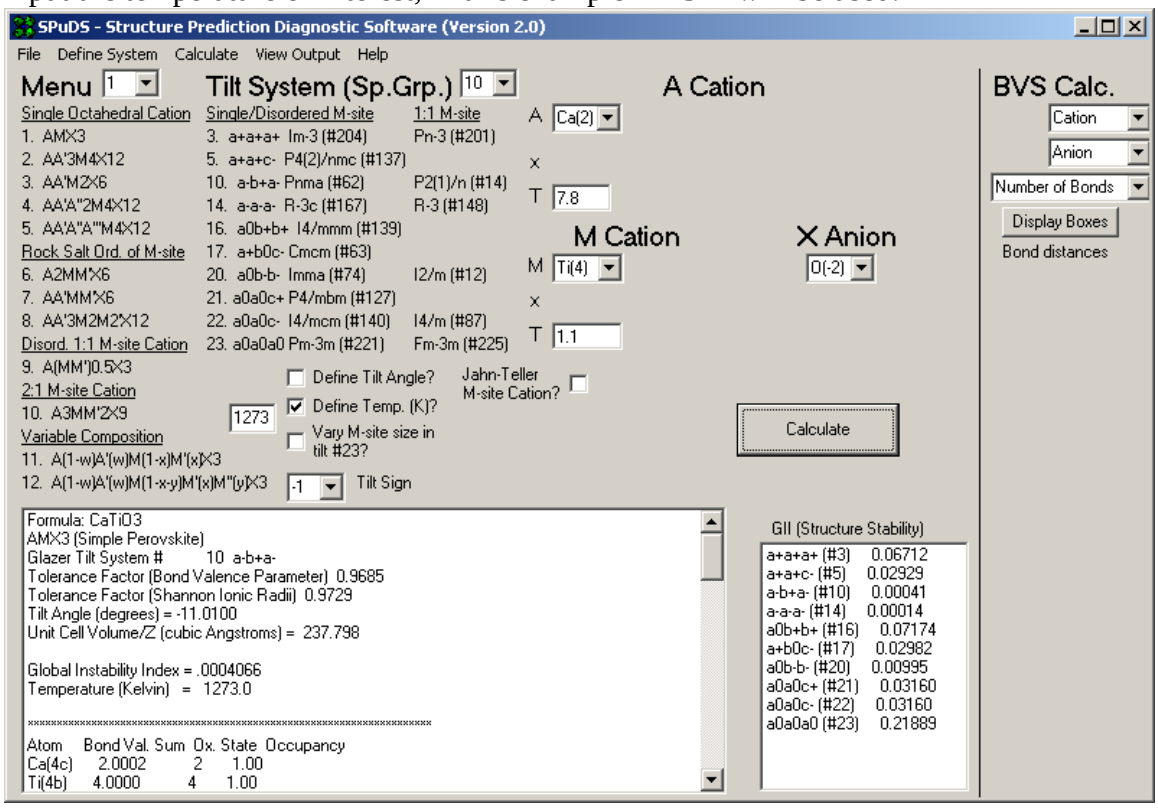
SPuDS has the capability to perform crystal structure calculations at variable temperatures. Temperature dependent bond valence parameters are based on ideas presented in Brown, Dabkowski and McCleary (1997). The dR/dT parameters used in the calculation of variable temperature bond valence parameters have units of Å K^{-1}. These parameters modify the bond valence parameter R_o (Brown, 2004) as a function of temperature using

$$R_o^T = R_o + (dR/dT)\Delta T$$

The values input into SPuDS are given in units of **x10^5**, *i.e.* the user inputs "7.8" into the text box for the temperature parameter for an A(2+). The default temperature is 298 K, and using this temperature as the input for the text box, results in no requirement for values in the "T" text boxes. Default temperature parameters values were obtained by approximation to Fig. 5 in Brown, Dabkowski and McCleary (1997). Values may need to be changed for each system investigated to accurately reflect the expansion of the bonds with an increase in temperature.

Oxidation State	A-site (dR/dT ×10^5)	M-site (dR/dT)
1	8	5
2	7.8	1.9
3	4.5	1.5
4	-	1.1
5	-	0.9
6	-	0.8

A sample calculation is shown for $CaTiO_3$. Check the box "Define Temp. K" and input the temperature of interest, in this example 1273 K will be used.



Note that the octahedral tilt angle decreased from -14.6 degrees to -11.01 degrees. SPuDS predicted fractional coordinates are given below for a calculation at a temperature equal to 1273 K.

****

Space Group: Pbnm (#62)
Lattice Parameters (Angstroms)
a = 5.4854
b = 5.5542
c = 7.8051

Atom	Site	x	y	z
Ca	4c	0.5049	0.5180	0.2500
Ti	4b	0.0000	0.5000	0.0000
O	4c	0.4438	-0.0062	0.2500
O	8d	0.7219	0.2774	0.0281

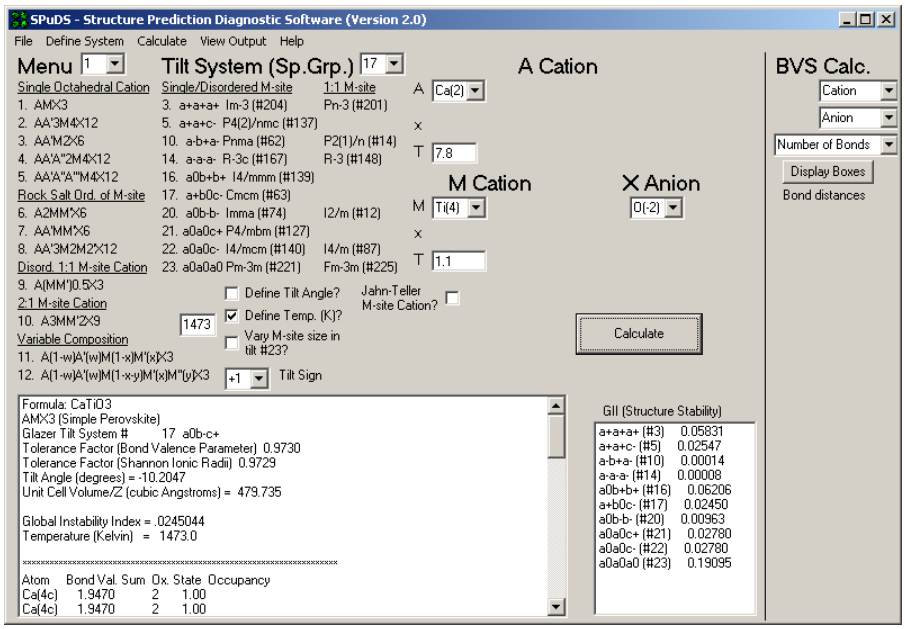
****

This may be compared to a high temperature diffraction experimental study of $CaTiO_3$ at 1273 K by Kennedy *et al*, 1999 shown below. Cell transformations are shown in the Appendix.

Atom	Site	x	y	z
Ca	4c	0.503(1)	0.519(1)	0.2500
Ti	4b	0.0000	0.5000	0.0000
O	4c	0.445(1)	-0.008(1)	0.2500
O	8d	0.7177(5)	0.2802(5)	0.0286(4)

Compare to the SPuDS predicted values, illustrating close agreement between refined and predicted values, even at 1273 K.

Now consider a phase transition. Calculate the crystal structure of $CaTiO_3$ at 1473 K, but change the space group to *Cmcm*, which is tilt system 17 ($a^+b^0c^-$). An out of phase tilt is no longer present compared to the low temperature crystal structure.



SPuDS predicted fractional coordinates for $CaTiO_3$ at 1473 K in space group *Cmcm* are:

****

Space group Cmcm (#63)
Lattice Parameters (Angstroms)
a = 7.7866
b = 7.8492
c = 7.8492

Atom	Site	x	y	z
Ca	4c	0.0000	0.4894	0.2500
Ca	4c	0.0000	-0.0081	0.2500
Ti	8d	0.2500	0.2500	0.0000
O	8e	-0.2187	0.5000	0.0000
O	8f	0.0000	0.2184	0.0316
O	8g	0.2818	0.2520	0.2500

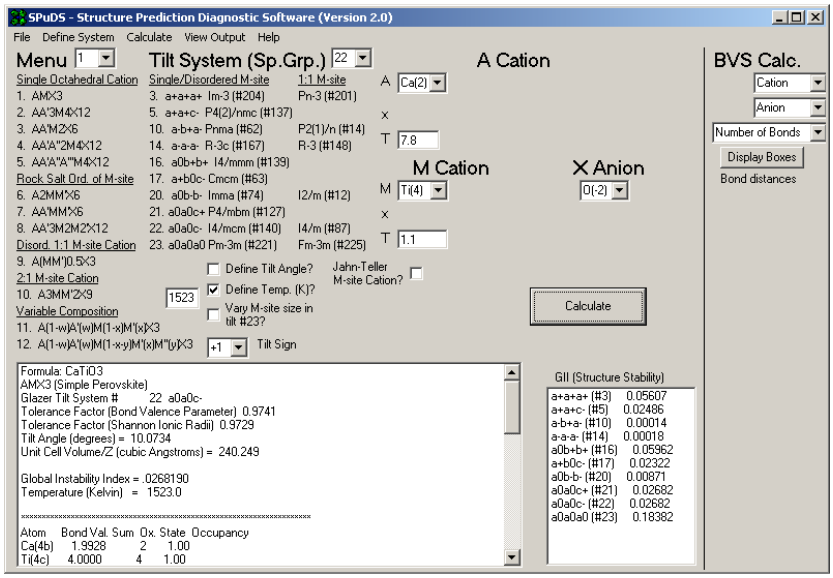
****

The refined fractional coordinates from Kennedy et al, 1999 are:

****

Atom	Site	x	y	z
Ca	4c	0.0000	0.505(5)	0.2500
Ca	4c	0.0000	-0.019(4)	0.2500
Ti	8d	0.2500	0.2500	0.0000
O	8e	-0.222(2)	0.5000	0.0000
O	8f	0.0000	0.226(2)	0.032(1)
O	8g	0.280(2)	0.251(2)	0.2500

Proceeding to higher temperatures (1523 K) another phase transition occurs to space group I4/mcm ($a^0a^0c^-$). The in-phase tilt is no longer present.



SPuDS predicted structural parameters are:

****

Space group I4/mcm (#140)
Lattice Parameters (Angstroms)
a = 5.5098
c = 7.9140

Atom	Site	x	y	z
Ca	4b	0.0000	0.5000	0.2500
Ti	4c	0.0000	0.0000	0.0000
O	4a	0.0000	0.0000	0.2500
O	8h	0.2056	0.7056	0.0000

****

Experimental refined structural parameters (Kennedy et al, 1999) are:

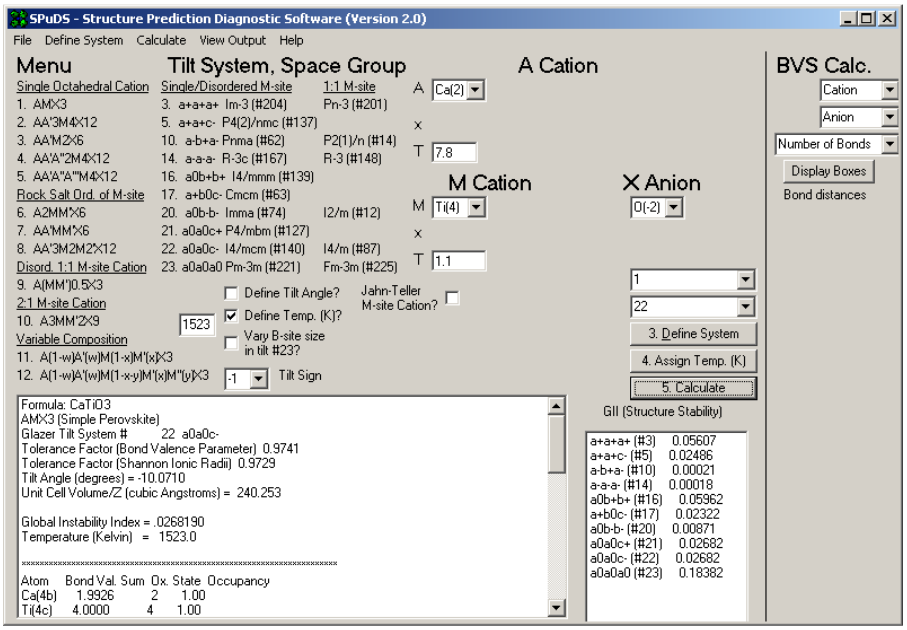
****

Space group I4/mcm (#140)
Lattice Parameters (Angstroms)
a = 5.4938(2)
c = 7.7815(3)

Atom	Site	x	y	z
Ca	4b	0.0000	0.5000	0.2500
Ti	4c	0.0000	0.0000	0.0000
O	4a	0.0000	0.0000	0.2500
O	8h	0.2783(5)	0.7783(5)	0.0000

****

Note the apparently significant difference in the O position on site 8h. This is because the octahedral tilting may be arbitrarily positive or negative. In the default case, the crystal structure has a positive tilt angle. Check the box "Define tilt angle" and change Tilt Sign from +1 to -1, then recalculate the crystal structure. (*Note: this feature does not work in all tilt systems in the current version of SPuDS, but can be added upon request.)*



Note the tilt angle was +10.07 degrees and is now -10.07 degrees. The crystal structure parameters are now:

****

Space group I4/mcm (#140)
Lattice Parameters (Angstroms)
a = 5.5098
c = 7.9140

Atom	Site	x	y	z
Ca	4b	0.0000	0.5000	0.2500
Ti	4c	0.0000	0.0000	0.0000
O	4a	0.0000	0.0000	0.2500
O	8h	0.2944	0.7944	0.0000

****

At a temperature 1623 K, no octahedal tilting is present as detected by diffraction measurements. SPuDS was used to calculate the crystal structure for the simple primitive cubic perovskite at 1623 K. A lattice parameter of 3.8933(1) Å was determined by Kennedy *et al*, 1999, with the atom positions equivalent. The crystal structure parameters are shown next.

****

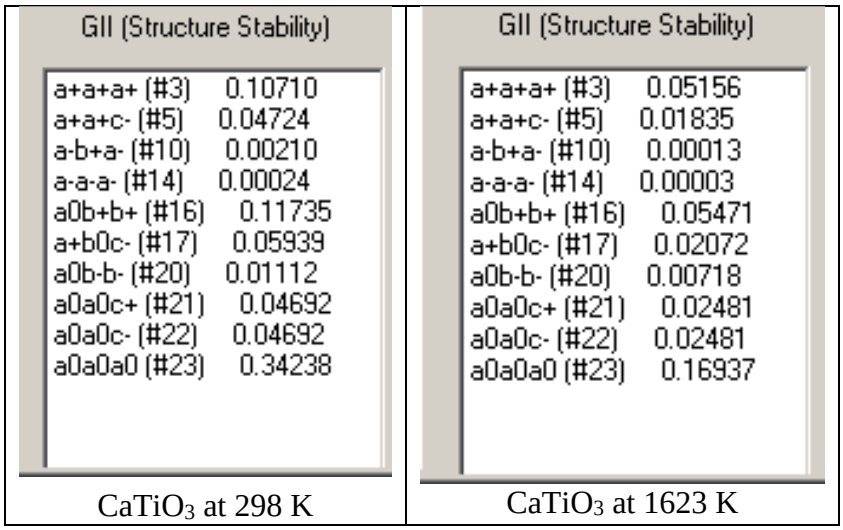
Space group Pm-3m (#221)

Lattice Parameters (Angstroms)
a = 3.9592

Atom	Site	x	y	z
Ca	1b	0.5000	0.5000	0.5000
Ti	1a	0.0000	0.0000	0.0000
O	3d	0.0000	0.0000	0.5000

****

Comparison of the GII can give some illustration of the phase transitions present in $CaTiO_3$. The A-site cation increases in size relative to the higher valent octahedral ions. The effective tolerance factor increases, making the less tilted (and untilted) phases less unstable compared to tilt system #10 ($a^-b^+a^-$, Pnma).



$CaTiO_3$ at 298 K | $CaTiO_3$ at 1623 K

Of course the true physics and chemistry is much more complicated than presented here, but nonetheless it may be useful to understanding phase transitions in perovskites. The accuracy of the fractional coordinates illustrate how SPuDS may be used to generate starting structure models in the course of structurally characterizing materials and also in analyzing known data.

2.5 Disordered Crystal Structure Calculation and Variable Composition

SPuDS has the capability to calculate disordered crystal structures with multiple A-site and multiple M-site cations for tilt system #10 $a^-a^-b^+$ (space group *Pnma/Pbnm*) and #22 $a^0a^0c^-$ (space group *I4/mcm*). In its current form, reliable results are only available for #10 and #22. Use menu 9, 11 or 12 for 1:1 disordered M-site, two A and two M-site, and two A and three M-site cations, respectively. Simple tilt system #10 has

only one crystallographic M-site. An *M-X* bond distance is calculated according to the following equations.

$$b = b(1)*bcomp(1) + b(2)*bcomp(2) + b(3)*bcomp(3)$$

A new **b** constant is calculated equal to the weighted average of the three b constants b(1-3), where bcomp(1-3) is the normalized fractional occupancy.

$$d = (rb(1)*bcomp(1) + rb(2)*bcomp(2) + rb(3)*bcomp(3)) - b*LOG(+ [oxb(1)*bcomp(1) + oxb(2)*bcomp(2) + oxb(3)*bcomp(3)]/6.)$$

The new bond distance is calculated using the equation above. This weighting scheme has a tendency to result in average bond valence sums of the M-site ions to have larger than ideal average values.

2.6 Jahn-Teller and Octahedral Distortions

2.6.1 Disordered M-site

Calculation of the crystal structures of compounds containing octahedral distortions is possible in SPuDS. One only needs to check the appropriate box for Jahn-Teller M-site. In its current form, only tilt system number 10 ($a^+b^-b^-$) is supported. Three boxes should appear (x,y,z).

The description of the Jahn-Teller distortion in combination with the Jahn-Teller distortion is achieved by applying equations of octahedral tilting to distorted octahedra, while still retaining nearly 90° O-M-O bond angles. Equations describing the oxygen fractional positions based on octahedral tilt angle are obtained in a similar method as for undistorted octahedra, but are more complicated.

Three bond distance factors (x, y, z) are included to modify the magnitude of the octahedral distortion. Starting values are x = -0.1, y = -0.04, z = 0.18. These values were chosen to approximate the distortion observed of Mn^{3+}. The resulting Mn-O bond distances are 1.9765 Å, 1.9194 Å, and 2.1925 Å, which gives a bond valence sum equal to 3.036 v.u. for Mn^{3+}. The experimental crystal by Rodriguez-Carvajal et al. (1998) has Mn-O bond distances at room temperature of 1.9680(3) Å, 1.907(1) Å, and 2.178(1) Å.

The bond distance factors influence the bond distances in the following way. A negative value shortens the M-O bond, whereas as positive value lengthens the M-O bond. Changing 'x' most strongly influences the M-O2 bond, 'y' the M-O1 bond, and z the M-O3 bond in the order the M-O bonds are listed in the output file. An example calculation is shown below for $LaMnO_3$ using the default (-) tilt angle .

Bond Distance Factors

x	y	z	Mn-O1 (×2)	Mn-O2 (×2)	Mn-O3 (×2)	BVS (v.u.)
0	0	0	2.0165	2.0165	2.0165	3.00
0	0	0.18	2.0165	2.0191	2.1926	2.61
0	-0.05	0	1.9665	2.0165	2.0165	3.14
-0.05	0	0	2.0166	1.9669	2.0159	3.14

-0.1	*-0.04*	*0.18*	*1.9765*	*1.9194*	*2.1925*	*3.04*
Additional examples						
-0.05	-0.04	0.18	1.9765	1.9692	2.1926	2.87
-0.1	-0.08	0.22	1.9365	1.9198	2.232	3.09
-0.12	-0.02	0.18	1.9965	1.8996	2.1922	3.05
-0.1	-0.08	0.18	1.9365	1.9191	2.193	3.16

The orientation of the observed Jahn-Teller distortion is given using the default bond distance factors (-0.1, -0.04, 0.18). By changing the value of x from -0.1 to -0.05, the Mn-O2 bond is lengthened and the Mn bond valence sum decreases to 2.87. The magnitude of the distortion is adjustable by varying these three parameters.

Consider $La_{0.5}Ca_{0.5}Mn^{3+}_{0.5}Mn^{4+}_{0.5}O_3$, with Mn^{4+} that often occupies a symmetric octahedral coordination environment. In the disordered case, the magnitude of the Jahn-Teller distortion may be expected to be reduced. Using the bond distance factors (-0.07, -0.025, 0.12) the resulting crystal structure would have Mn-O bond distances of 1.9309 Å, 1.8872 Å, and 2.0473 Å and bond valence sums of 3.53 v.u for Mn^{3+} and 3.47 v.u. for Mn^{4+} on the disordered M-site. This approach has the effect of averaging the distortion around the M-site. The magnitude of the octahedral distortion is difficult to estimate, and is left up to the user to generate the appropriate octahedral distortion.

When should one use the Jahn-Teller distortion option? There is no simple answer. For example, $La_{0.5}Ca_{0.5}MnO_3$ (Radaelli et al, 1997) has symmetric octahedra at T = 300 K, whereas at 1.5 K a short Mn-O bond is formed. Obviously in this case, a simulation of the room temperature structure would not need a Jahn-Teller distortion, whereas a low temperature crystal structure is better described by a distorted crystal structure. A starting point may be (x = 0, y = -0.05, z = 0), which give Mn-O bond distances of 1.9021 Å, 1.9521 Å, 1.9521 Å in good agreement with the experimental values of 1.9148(3) Å, 1.951(1) Å, and 1.959(1) Å. The calculated and experimental crystal structures (mirror image about ab-plane) are shown below in the *Pnma* setting at 1.5 K with the (-) tilt sign.

$La_{0.5}Ca_{0.5}MnO_3$	Experimental	SPuDS calculated
a (Å)	5.4466(3)	5.4917
b (Å)	7.5247(4)	7.5256
c (Å)	5.4763(3)	5.4320
La/Ca *x*	0.5195(3)	0.5155
La/Ca *z*	0.5036(2)	0.4999
O(4c) *x*	-0.0095(4)	-0.0053
O(4c) *z*	0.4355(2)	0.4488
O(8d) *x*	0.2720(2)	0.2757
O(8d) *y*	0.0337(1)	0.0270
O(8d) *z*	0.7271(2)	0.7237

2.6.2 Ordered M-site

Calculation of a charge ordered type structure is also possible. Consider the calculation the crystal structure of $La_{0.5}Ca_{0.5}Mn^{3+}_{0.5}Mn^{4+}_{0.5}O_3$ with hypothetically rock-

salt type ordering Mn^{3+} and Mn^{4+}. This feature is in testing, but through appropriate substitution of x,y,z bond distance factors, a crystal structure with one Jahn-Teller distorted and one octahedrally symmetric ion may be generated. The correct orientations of the long, medium, and short M-O bonds need to be obtained to match that observed experimentally. Note that more distortion of the octahedral angles (O-M-O) is expected with an increased distortion of the M-O bond lengths on a single octahedral site in the ordered, as opposed to the disordered case where the distortions are cooperative.

Bond Distance Factors

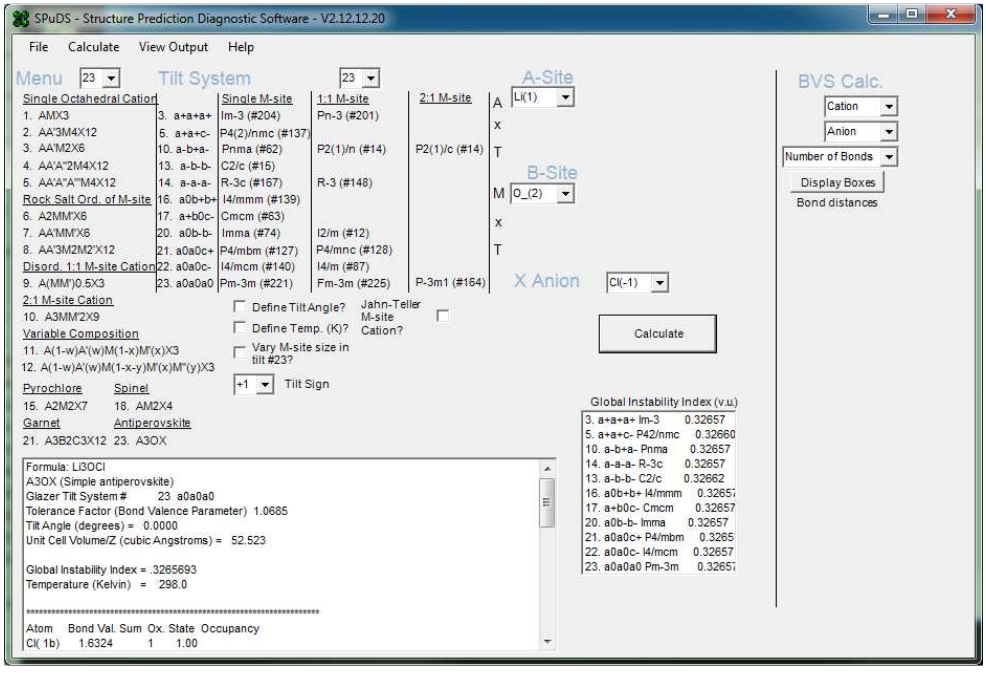
x	y	z	Mn-O1 (×2)	Mn-O2 (×2)	Mn-O3 (×2)	BVS M1,2 (JT)(v.u.)
0	0	0	2.0212	2.0118	2.0174	3.00
			1.8991	1.9068	1.902	4.00
0	0	0.18	*2.1234*	*2.0896*	2.0209	2.56
			1.9016	1.9064	1.9052	3.99
0	0.1	0	2.0248	*2.12*	*2.1142*	2.76
			1.8974	1.9085	1.9018	4.01
0.1	0	0	*2.0677*	*2.0626*	2.0196	2.75
			1.8961	1.9113	1.904	3.99
-0.1	-0.04	0.18	2.0744	2.0407	1.9794	2.90
			1.9081	1.9047	1.9028	3.98

2.7 Pyrochlores

Structure prediction for simple $A_2B_2O_7$ pyrochlores is available. The tolerance factor calculation is based on that of (Isupov, 1958).

2.8 Anti-perovskites

Structure prediction for anti-perovskites is available for formulas of the type A_3OX. The input requires the X and A-sites to be reversed. Sample input is shown below.



2.9 Frequently Asked Questions

Q. Why does the (#10) $a^-b^+a^-$ tilt system, space group *Pnma*, only have a single tilt angle?

A. The $a^-b^+a^-$ tilt system has both in phase and out of phase octahedral tilting. SPuDS uses the assumption that the octahedra do not undergo a distortion if allowed to remain symmetric (equidistant *M-X* distances, 90° or 180° *X-M-X* bond angles), which requires the in-phase and out-of-phase tilt angles to be coupled to maintain regular octahedra. More details and the equations that relate the primary and secondary tilt angles are found in section 3.2.2 of this user manual, section 3 in the SPuDS paper (Lufaso and Woodward, *Acta Cryst.* (2001), B**57**, 725-738) and sequence (iv) on page 3806 in O'Keeffe and Hyde, *Acta Cryst.* (1977), B**33,** 3802-3813.

Q. Why does the (#14, $a^-a^-a^-$) R-3c always give the lowest GII, but Pnma (#10, $a^-b^+a^-$) are more often observed experimentally?

A. The symmetric tilting about the octahedral face results in the crystal structure obtaining the lowest GII, but does not consider that unfavorably short A-O and O-O interactions may occur in the hypothetical crystal structure. Chapter 6 and figure 6.4 of 'The Chemical Bond in Inorganic Chemistry; Oxford; 2002 by I.D. Brown give some useful guidelines for typical O-O distances. Large tilt angles in (#14, a-a-a-) space group *R-3c* result in three very short A-O bonds, which are not favorable compared to a more symmetric coordination environment for the A-site cation. For example, the hypothetical crystal structure of $CaZrO_3$ in space group *R-3c* (#14, a-a-a-) has 3 Ca-O bonds of 2.22 Å with valences of 0.50 v.u. each. That means 75% (1.50 v.u./2 v.u.) of the Ca^{2+} bonding requirements is satisfied with only 3 bonds. Contrast that to the three short Ca-O bonds of $CaZrO_3$ in space group Pnma (#10, $a^-b^+a^-$), which are 0.366 v.u., 0.324 v.u., and 0.280 v.u. for a total of 0.97 v.u., which is less that 50% of the Ca^{2+} bonding.

The above example illustrates why space group Pnma perovskites (#10, $a^-b^+a^-$) are observed more often than (#14, a-a-a-) space group R-3c perovskites, even though the GII is lower for R-3c (0.00018 v.u.) compared to Pnma (0.01413 v.u). The GII is just an indication of the relative structure stability, but does not contain information regarding the bonding or if unstable bond distances are involved. Below a certain threshold value of the GII, any tilt system may be stable and additional factors need to be considered, such as the A-O bonding described above.

Q. The 40 atom *C*2/*c* cell is used to describe the $a^-b^-b^-$ tilting as opposed to the 20 atom I2/a cell. Why?

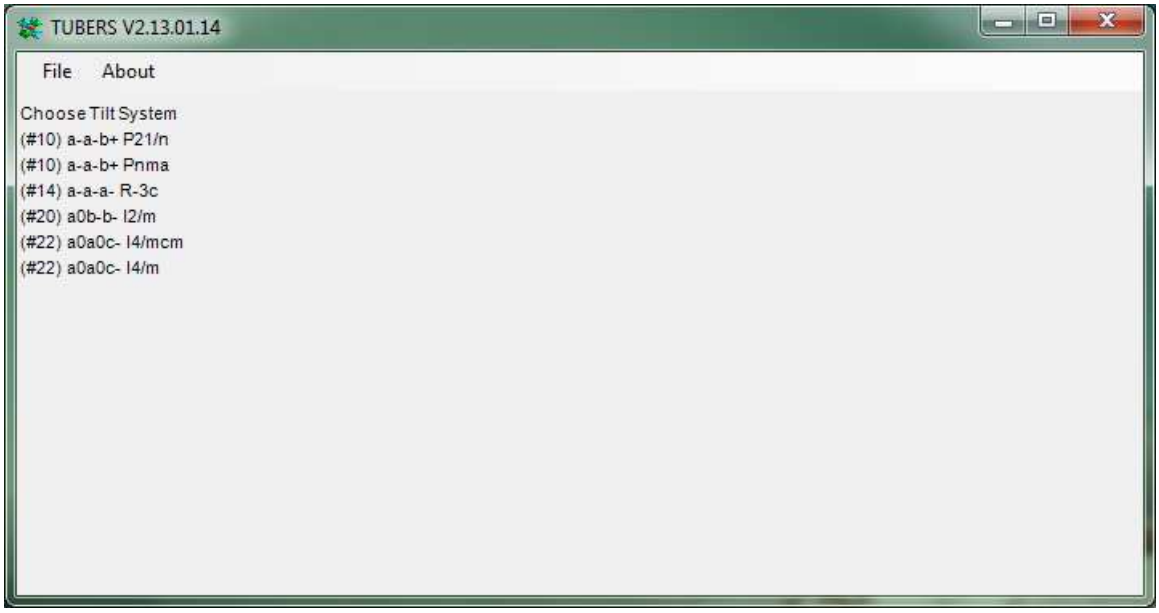
A. The *C*2/*c* setting was the one originally used by Glazer (1972) and also by Howard and Stokes (1998). The setting chosen in SPuDS was used to give a structure similar to the *C*2/*c* setting of $BiMnO_3$ (ICSD 56842). The structure prediction for the rarely observed $a^-b^-b^-$ tilt system is still being tested. The octahedral bond distances do not quite remain ideal. If you have a specific interest in this tilt system, let me know and at some point I can revisit the code dealing with this subroutine. If the *I*2/*a* cell is more convenient, it might be a possibility to include that as well (like with the *Pnma* and *Pbnm* setting).

Chapter 3

Tilt Angle Calculation using TUBERS

3.1 Overview

TUBERS may be used to calculate the tilt angles of the octahedra from an experimental crystal structure. This feature is only available for tilt systems with space groups $P2_1/n$, *Pnma*, *R*-3*c*, *I*2/*m*, *I*4/*mcm*, and *I*4/*m* in the current *TUBERS* version. Contact the author (michael.lufaso@unf.edu) for more details or to request a particular tilt system.



3.2 Single M-site perovskites

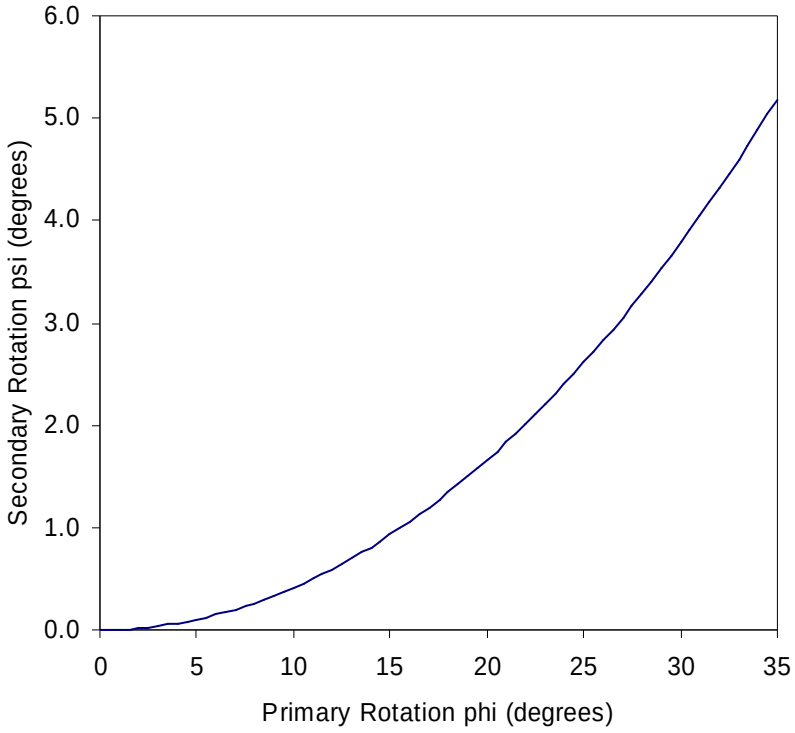
Some tilt systems have direct equations to go from fractional coordinate to tilt angle. In this case, the program will prompt for the fractional coordinate, which must be near the general position given in the prompt.

3.2.1 #22 ($a^0a^0c^-$) space group *I4/mcm*

The fractional coordinate is the only input required for calculating the octahedral tilt angle in space group I4/mcm perovskites.

3.2.2 **#10 (a^-b+a^-) space group *Pnma***

The calculation of the tilt angle in *Pnma* requires only the fractional positions of the O atoms. The fractional positions of the anions must match the setting used for the SPuDS calculations. It is necessary to convert to *Pnma* setting from any other setting (e.g. *Pbnm*). The tilt angle given is obtained by solving the equations given by O'Keeffe & Hyde (1977) for the *z* fractional coordinate of O at Wyckoff position 4c and the *x*, *y*, and *z* fractional coordinates for the O position at the Wyckoff position 8d. The resulting tilt angle is given as φ in the TUBERS calculation. A secondary tilt ψ is required. The relationship between φ and ψ is given below and full details may be found in O'Keeffe & Hyde (1977). The average φ octahedral tilt angle is also given.



3.3 Multiple M-site perovskites

Calculation of the octahedral tilt angle is possible for tilt systems #10 ($a^-a^-b^+$) space group *P2₁/n* and #20 ($a^0b^-b^-$) space group *I2/m*.

3.3.1 SPuDS text version [#22 ($a^0a^0c^-$) and #14 ($a^-a^-a^-$)]

(This version of SPuDS is being phase out by TUBERS)

The text based version of SPuDS is required for calculation of octahedral tilt angle for tilt systems 22 ($a^0a^0c^-$) and 14 ($a^-a^-a^-$). Equations used to calculate the fractional coordinate from the tilt angle are complex. Matrix methods are used to obtain the equation for fractional coordinates based on M-X bond distances and octahedral tilt angles. The fractional coordinate equations incorporate the lattice parameter into the equation in terms of the bond distances and tilt angle. Therefore obtaining an equation for the tilt angle from the fractional coordinate and lattice parameters is not trivial.

Instead, SPuDS takes the average M_1-X and M_2-X bond distance obtained from the experimental crystal structure as input. The fractional coordinates are then serially calculated for a variety of tilt angles into a file named *tltangle.txt*. Inspection of the file allows one to obtain the tilt angle by searching for a fractional coordinate near the experimental crystal structure value. The fractional coordinates must be refined or converted to approximately the same position.

General
From the experimental crystal structure calculate the mean M_1-O and M_2-O bond distances.

Execute text version SPuDS, choose menu 13.
Type tilt system number of interest.
Type number corresponding to simple or ordered.
Enter the mean M_1-O bond distance.
Enter the mean M_2-O bond distance.

SPuDS will execute and terminate.

Go to the SPuDS folder and open tltangle.txt, search for each fractional coordinate nearest the experimental value and record the tilt angle. The average for each anion fractional coordinate is the experimental octahedral tilt angle.

Note, distortions of the octahedra are the cause for discrepancy in the tilt angle. It is up to the user to weigh each the accuracy of each fractional coordinate and discard any outliers in order to obtain meaningful results.

3.3.2 TUBERS [#10 ($a^-a^-b^+$) space group *P2₁/n*]

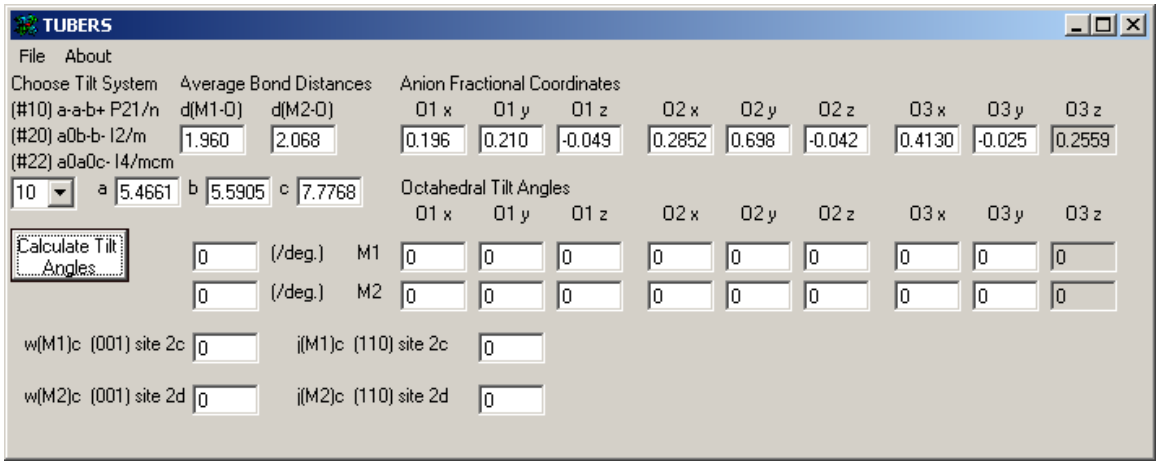
The software program *TUBERS* allows calculation of octahedral tilt angles for ordered perovskites in space groups *P2₁/n*. The calculation algorithm for determining the octahedral tilt angle(s) involves using the equations of tilt that SPuDS uses to calculate fractional coordinates based on *M-X* bond distances and the octahedral tilt angle. In addition, the calculation of the tilt angles *w* [rotation about (001) of the aristotype perovskite] and *j* [rotation about (110) of the aristotype perovskite] as described by Groen *et al.* (1986) are included for comparison. The formulas for $w(B)_c$ and $w(B')_c$ appear to be swapped in the original paper, and have been switched to agree with the tilt angles obtained in the original paper.

TUBERS utilizes the equations from the SPuDS software to calculate the tilt angles based on the fractional positions and average M-O bond distances. This method of

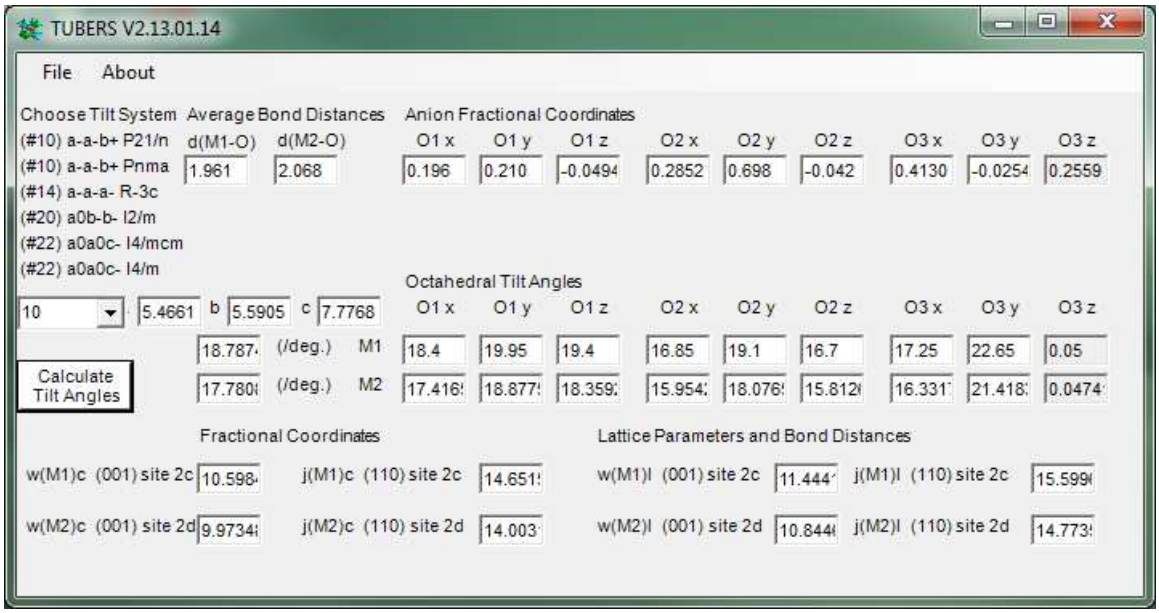
calculating the octahedral tilt angle has an advantage over the method that separates the (110) and (001) tilts, because it ensures the octahedra retain approximately corner-sharing connectivity. The tilt angle calculated by *TUBERS* links the inherent coupling of the octahedral tilts about the [001] and [110] axes. For example, the $a^-a^-b^+$ tilt system is based on a tilt about the [110] is followed by secondary correction tilt about the [001] axis, similar to the one made by O'Keeffe, M. & Hyde, B.G. (1977) to maintain corner connectivity of octahedra in the simple AMX_3 perovskite (space group *Pbnm/Pnma*). Two different cation sites in the $P2_1/n$ crystal structure and different size octahedra make the equations describing the anion fractional positions very complicated. Simplified equations were solved by matrix algebra methods; however each equation is several pages in length. Because of the complexity, the equations are not repeated here. The interested reader can find the complete equations in the appendix of Lufaso, M.W. Ph. D. (2002) dissertation at http://www.ohiolink.edu/etd/view.cgi?osu1039132858.

In order to calculate the octahedral tilt angles in space group $P2_1/n$ ($a^-a^-b^+$), the required user input are the average M_1-O (Wyckoff position 2c) and M_2-O (Wyckoff position 2d) bond distances, the anion (Oxygen) fractional coordinates, and lattice parameters. The fractional coordinates must approximately match the sample given in the software. Use the International Tables for Crystallography to generate the additional positions if the approximate fractional coordinates do not match. A shift of all atoms in the unit cell will be necessary if the Wyckoff sites of the octahedral cations are 2a and 2b, rather than 2c and 2d as required by the equations used in TUBERS. Approximate unit cell dimensions are $a \approx \sqrt{2}a_p$, $b \approx \sqrt{2}a_p$ and $c \approx 2a_p$, where a_p is the primitive unit cell length. The cation fractional positions are M(2c) (0, ½,0), M′(2d) (½, 0, 0) and A(4e) (*x*, *y*, *z*) where $x \approx ½$, $y \approx ½$ and $z \approx ¼$. Anion fractional positions for three cations are X(4e) (*x*, *y*, *z*) where ($x \approx ¼$, $y \approx ¼$ and $z \approx 0$; $x' \approx ¼$, $y' \approx ¾$ and $z' \approx 0$; $x'' \approx ½$, $y'' \approx 0$ and $z'' \approx ¼$).

An example calculation of octahedral tilt angles is performed using an experimental crystal structure of Nd_2TiMgO_6 (Groen *et al.*, 1986). Average bond distances were calculated and input into *TUBERS*. By convention, M1-O is the average M-O bond distance for the M-site cation on position 2c, whereas M2-O is for the M-site cation on position 2d. Given oxygen fractional coordinates, without ESD's, are O1 (0.1960, 0.2100, -0.0494), O2(0.2852, 0.6980, -0.0420), and O3 (0.4130, 0.9746, 0.2559). Note that the y-position of O3 needs shifted by -1 to match the required input. The resulting fractional coordinates are now O1 (0.1960, 0.2100, -0.0494), O2(0.2852, 0.6980, -0.0420), and O3 (0.4130, -0.0254, 0.2559). These fractional coordinates, average bond distances, and lattice parameters were input and are shown below.

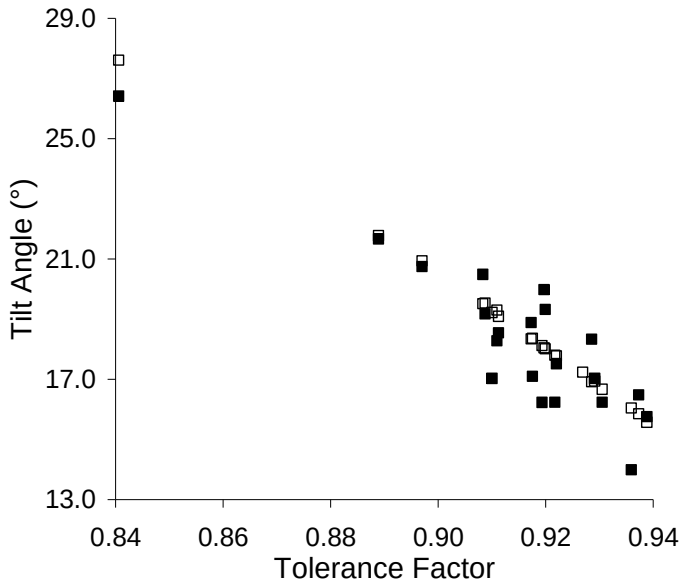

TUBERS
File About
Choose Tilt System
(#10) a-a-b+ P21/n
(#20) a0b-b- I2/m
(#22) a0a0c- I4/mcm
Average Bond Distances
d(M1-O) d(M2-O)
1.960 2.068
Anion Fractional Coordinates
O1 x O1 y O1 z O2 x O2 y O2 z O3 x O3 y O3 z
0.196 0.210 -0.049 0.2852 0.698 -0.042 0.4130 -0.025 0.2559
10 a 5.4661 b 5.5905 c 7.7768
Octahedral Tilt Angles
O1 x O1 y O1 z O2 x O2 y O2 z O3 x O3 y O3 z
Calculate Tilt Angles
0 (/deg.) M1 0 0 0 0 0 0 0 0 0
0 (/deg.) M2 0 0 0 0 0 0 0 0 0
w(M1)c (001) site 2c 0
j(M1)c (110) site 2c 0
w(M2)c (001) site 2d 0
j(M2)c (110) site 2d 0

Tilt angles were calculated by pressing the 'Calculate Tilt Angles' button.


TUBERS V2.13.01.14
File About
Choose Tilt System
(#10) a-a-b+ P21/n
(#10) a-a-b+ Pnma
(#14) a-a-a- R-3c
(#20) a0b-b- I2/m
(#22) a0a0c- I4/mcm
(#22) a0a0c- I4/m
Average Bond Distances
d(M1-O) d(M2-O)
1.961 2.068
Anion Fractional Coordinates
O1 x O1 y O1 z O2 x O2 y O2 z O3 x O3 y O3 z
0.196 0.210 -0.0494 0.2852 0.698 -0.042 0.4130 -0.0254 0.2559
Octahedral Tilt Angles
10 5.4661 b 5.5905 c 7.7768
O1 x O1 y O1 z O2 x O2 y O2 z O3 x O3 y O3 z
18.787 (/deg.) M1 18.4 19.95 19.4 16.85 19.1 16.7 17.25 22.65 0.05
17.780 (/deg.) M2 17.416 18.877 18.359 15.954 18.076 15.812 16.331 21.418 0.0474
Calculate Tilt Angles
Fractional Coordinates
w(M1)c (001) site 2c 10.598
j(M1)c (110) site 2c 14.651
w(M2)c (001) site 2d 9.9734
j(M2)c (110) site 2d 14.003
Lattice Parameters and Bond Distances
w(M1)l (001) site 2c 11.444
j(M1)l (110) site 2c 15.599
w(M2)l (001) site 2d 10.844
j(M2)l (110) site 2d 14.773

The tilt angles of the [TiO_6] and [MgO_6] are 18.8° and 17.8°, respectively. Note the tilt angle calculated based on the position of O3z is significantly different. The position of atom O3z is insensitive to the octahedral tilt angle and is disregarded in the calculation of the average tilt angle. The average tilt angle is calculated with the other 8 oxygen anions. The spread of the tilt angles is present because of octahedral distortion of M_1-O and M_2-O bond lengths and O-M-O bond angles. Note the smaller ion undergoes a larger tilting in order to maintain corner-sharing connectivity. The tilt angles $w(M1)_c$, $w(M2)_c$, $j(M1)_c$ and $j(M2)_c$ are shown, in agreement with the values found in Groen *et al.*, 1986.

In general, there is close agreement between calculated and theoretical tilt angles from SPuDS simulations. A plot for multiple space group $P2_1/n$ perovskite compounds is shown in the next figure; with open squares SPuDS predicted average tilt angles and filled square average literature tilt angles.



3.3.3 TUBERS [#20 ($a^0b^-b^-$) space group *I2/m*]

The software program *TUBERS* allows calculation of octahedral tilt angles for ordered perovskites in space groups *I2/m*. The calculation algorithm is similar to that utilized for $P2_1/n$ perovskites. In this tilt system, only the average M1-O, M2-O bond distances and O fractional coordinates of O1x and O2z are required. The other fractional coordinates are not sensitive to the octahedral tilting, so are neglected in the calculation.

The octahedral cations are required to be on Wyckoff sites *2a* (0, 0, 0), (1/2, 1/2, 1/2) and *2d* (1/2, 1/2, 0) or (0, 0, 1/2). Consider an example Ba_2BiBiO_6 (Cox & Sleight, 1976) (ICSD CCode 87326). Average Bi^{3+}-O bond lengths are 2.276 Å and Bi^{5+}-O are 2.119. Anion fractional coordinates are O(4i) [0.0604(9), 0, 0.2608(17)] and O(8j) [0.2613(9), 0.2552(21), -0.0334(4)]. The resulting tilt angles are 9.9° for Bi^{3+}(2a) and 10.6° for Bi^{5+}.

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Appendix A

Conversion of *Pbnm*

****

Space Group: Pbnm (#62)
Lattice Parameters (Angstroms)
a = 5.4671(2)
b = 4.4823(2)
c = 7.7461(3)

Atom	Site	x	y	z
Ca	4c	0.003(1)	0.519(1)	0.2500
Ti	4a	0.0000	0.0000	0.0000
O	4c	-0.055(1)	-0.008(1)	0.2500
O	8d	0.2177(5)	0.2802(5)	0.0286(4)

****

Note that the Ti is located on site 4b in the SPuDS predicted crystal structure, whereas it is on the 4a site in the Kennedy *et al*, 1999 crystal structure. The site symmetry is -1 in both the 4a and 4b site, so shift the unit cell by (0.5, 0, 0). The resulting fractional coordinates are now:

Atom	Site	x	y	z
Ca	4c	0.503(1)	0.519(1)	0.2500
Ti	4b	0.5000	0.0000	0.0000
O	4c	0.445(1)	-0.008(1)	0.2500
O	8d	0.7177(5)	0.2802(5)	0.0286(4)

The equivalent positions for the 4b site in space group *Pnma* are (0,0,0.5), (0.5,0,0), (0,0.5,0.5) and (0.5,0.5,0), therefore the equivalent positions in *Pbnm* are (0.5,0,0), (0, 0.5,0), (0.5,0,0.5) and (0,0.5,0.5). We can rewrite the positions as:

Atom	Site	x	y	z
Ca	4c	0.503(1)	0.519(1)	0.2500
Ti	4b	0.0000	0.5000	0.0000
O	4c	0.445(1)	-0.008(1)	0.2500
O	8d	0.7177(5)	0.2802(5)	0.0286(4)

****

Space group Cmcm (#63)
Lattice Parameters (Angstroms)
a = 7.7642(6)
b = 7.7674(4)
c = 7.7667(4)

Atom	Site	x	y	z
Ca	4c	0.0000	0.505(5)	0.2500
Ca	4c	0.0000	-0.019(4)	0.2500
Ti	8d	0.2500	0.2500	0.0000
O	8e	0.278(2)	0.0000	0.0000
O	8f	0.0000	0.226(2)	0.032(1)
O	8g	0.280(2)	0.251(2)	0.2500

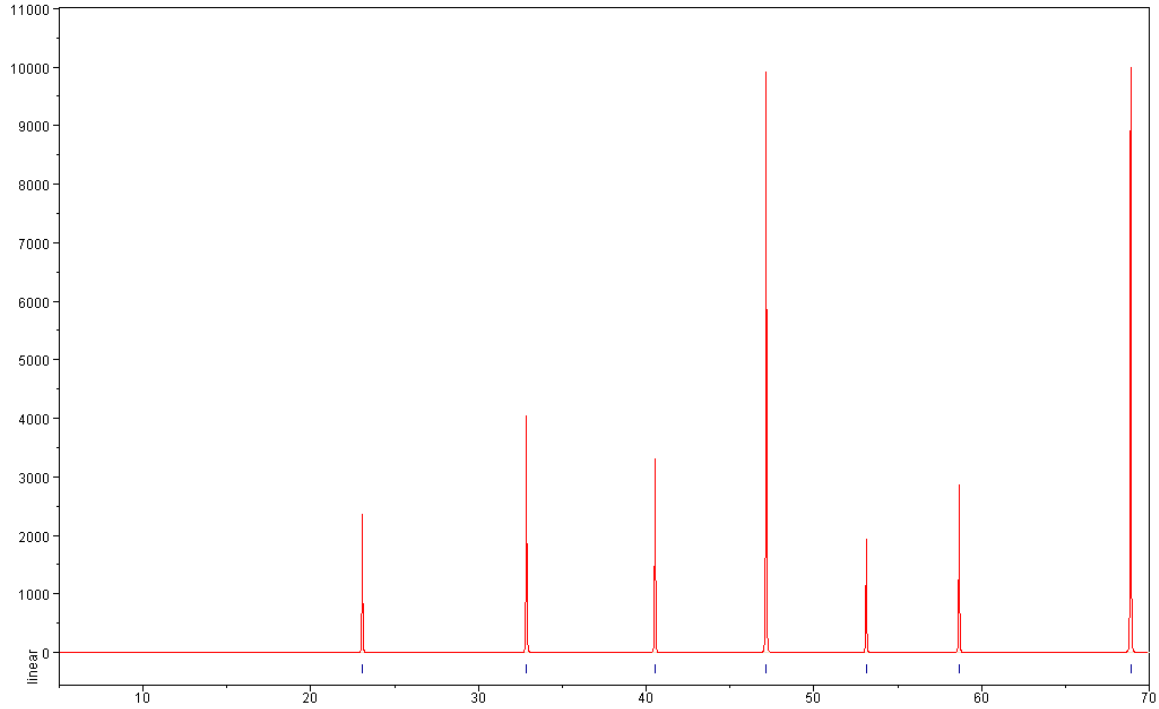
****

Note that O on site 8e are not easily comparable between the SPuDS and experimental crystal structure, so find equivalent positions. Site positions are (x, 0,0), (-x, 0, 0.5), (-x,0,0), and (x, 0, 1/2) combined with (0.5, 0.5, 0) to generate all 8 positions for the site. Adding (0.5, 0.5, 0) to the O at site 8e, generating the equivalent position, gives the following fractional coordinates after a shift of minus one unit cell in the *x* direction.

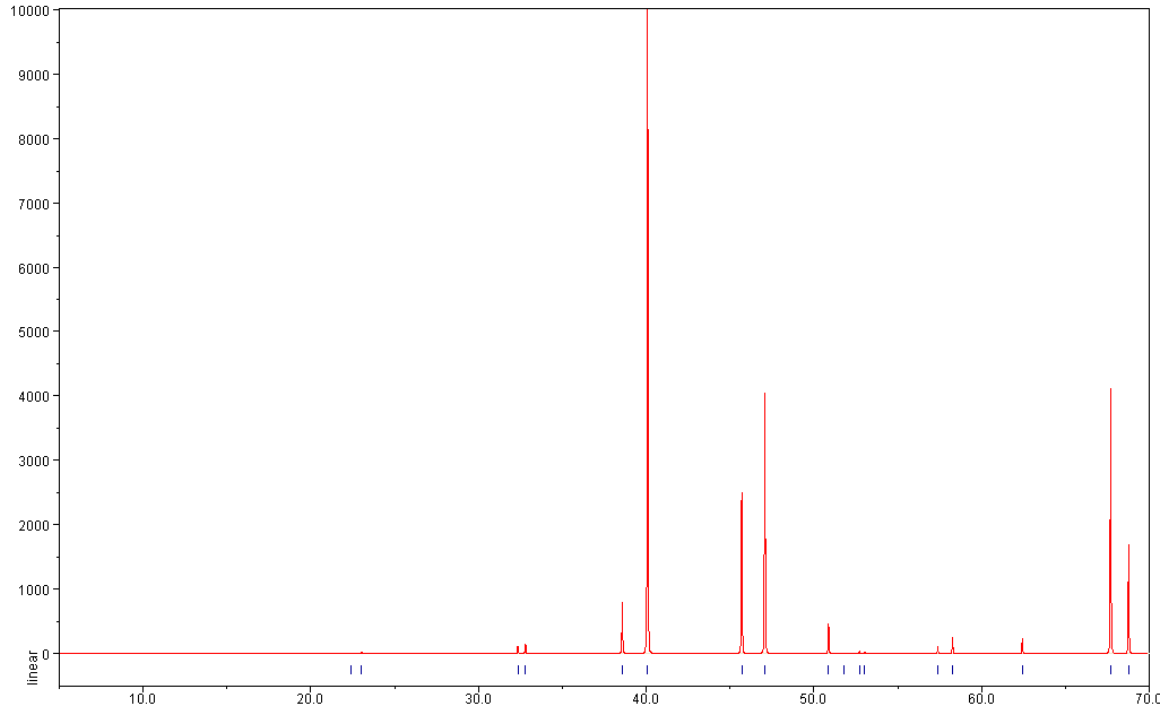
Appendix B

Neutron Powder diffraction simulations (λ = 1.5403 Å)

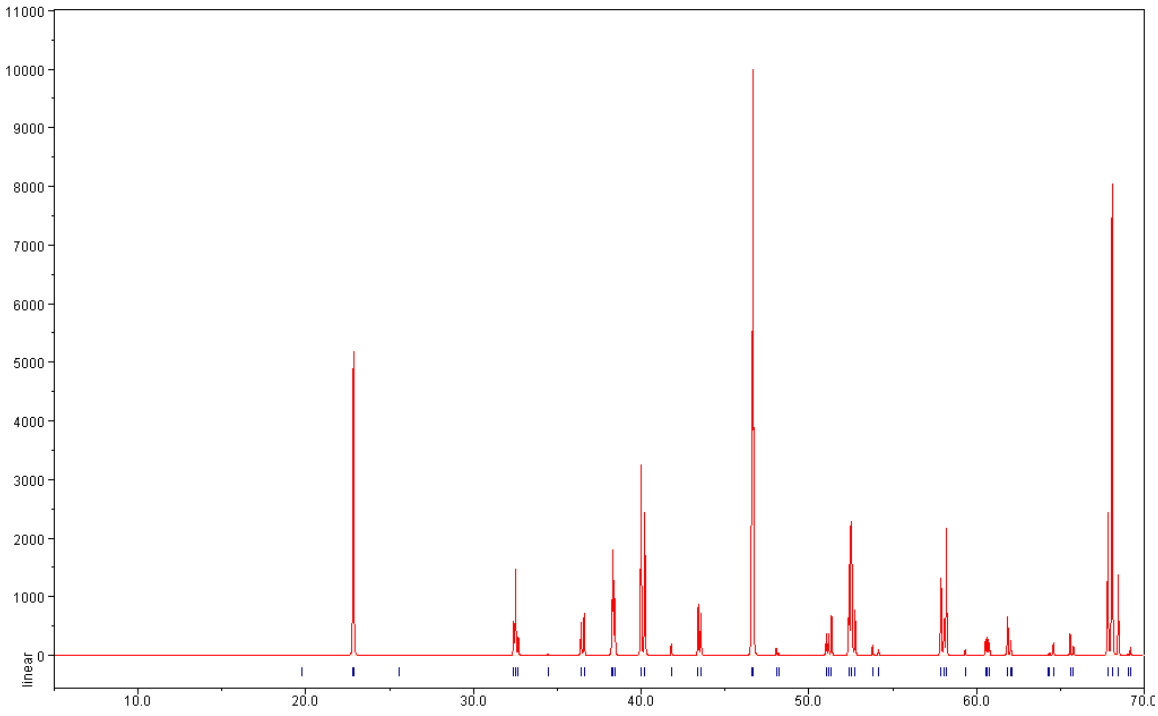
$SrFeO_3$ (Sp. grp. *Pm-3m*)



$Sr(Ti_{0.65}Fe_{0.35})O_{3-\delta}$ (Sp. grp. I4/mcm)



$NaTaO_3$ (Sp. grp. Pbnm)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9000
8000
7000
6000
5000
4000
3000
2000
1000
0
linear
10.0
20.0
30.0
40.0
50.0
60.0